Supporting Information

Accelerating Reaction Kinetics of Lithium-Oxygen Chemistry by Modulating Electron Acceptance-Donation Interaction in Electrocatalysts

Chuan Zhao [a], Jianping Long [a,*], Bo Zhou [a], Ruixin Zheng [a], Miao He [a], Runjing Li [a], Yu Pan [a], Anjun Hu [b] and Chaozhu Shu [a,*]

[a] College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, 1#, Dongsanlu, Erxianqiao, Chengdu 610059, Sichuan, P. R. China

[b] State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, 610054, Sichuan, PR China

* Corresponding author: czshu@imr.ac.cn; shuchaozhu13@cdut.edu.cn (Chaozhu Shu); longjianping@cdut.cn (Jianping Long).

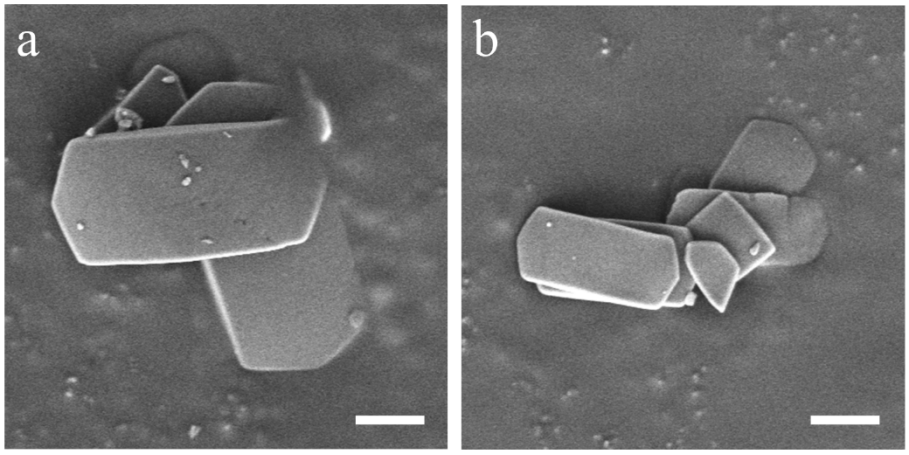

Figure S1. SEM images of (a) Zn ZIF, (b) $Zn_{0.6}Co_{0.4}$ ZIF. Scale bars, 1 μm for SEM.

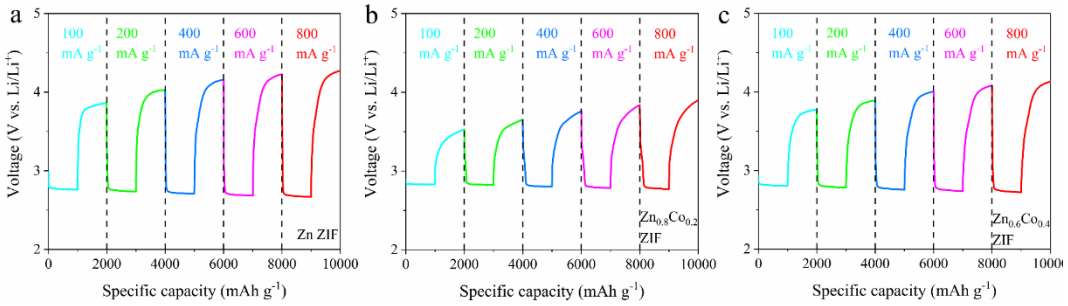

Figure S2. Rate capability of (a) Zn ZIF, (b) $Zn_{0.8}Co_{0.2}$ ZIF and (c) $Zn_{0.6}Co_{0.4}$ ZIF cathodes.

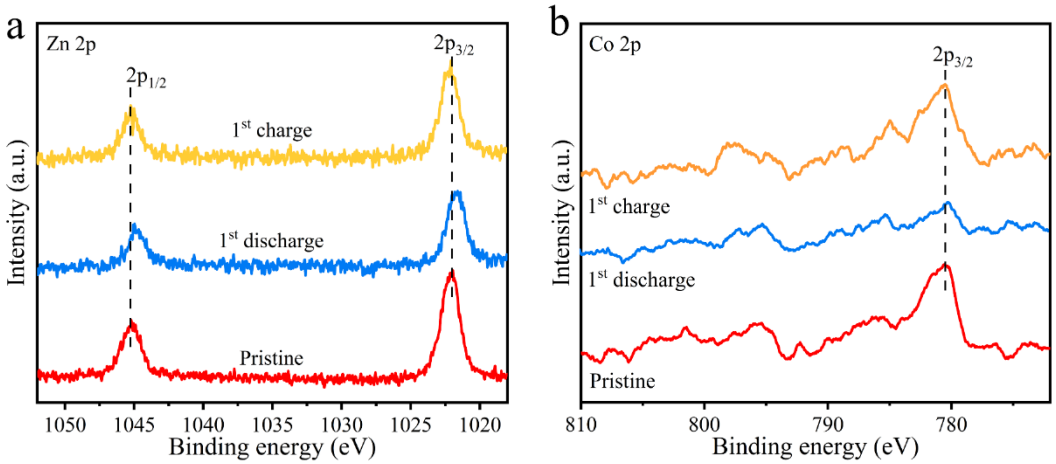

Figure S3. (a) Zn 2p and (b) Co 2p XPS for $Zn_{0.8}Co_{0.2}$ ZIF electrode at different states.

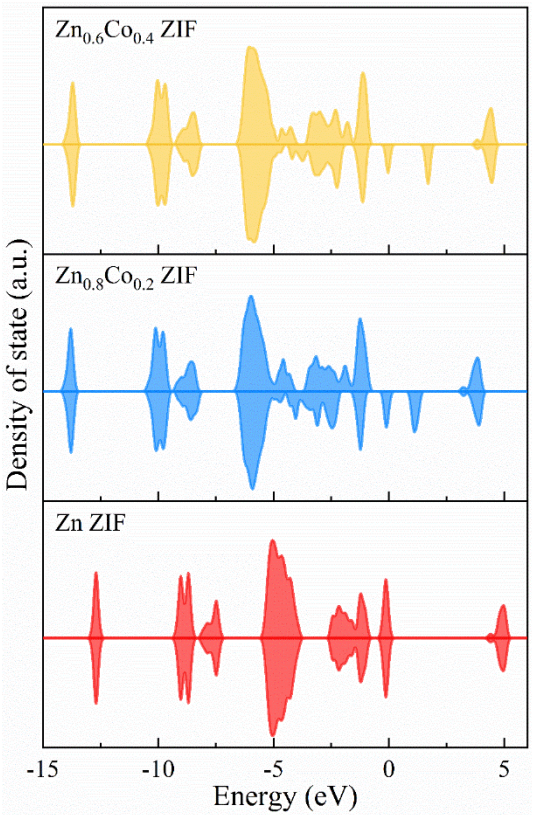

Figure S4. The total density of states for the Zn ZIF, $Zn_{0.8}Co_{0.2}$ ZIF and $Zn_{0.6}Co_{0.4}$ ZIF.

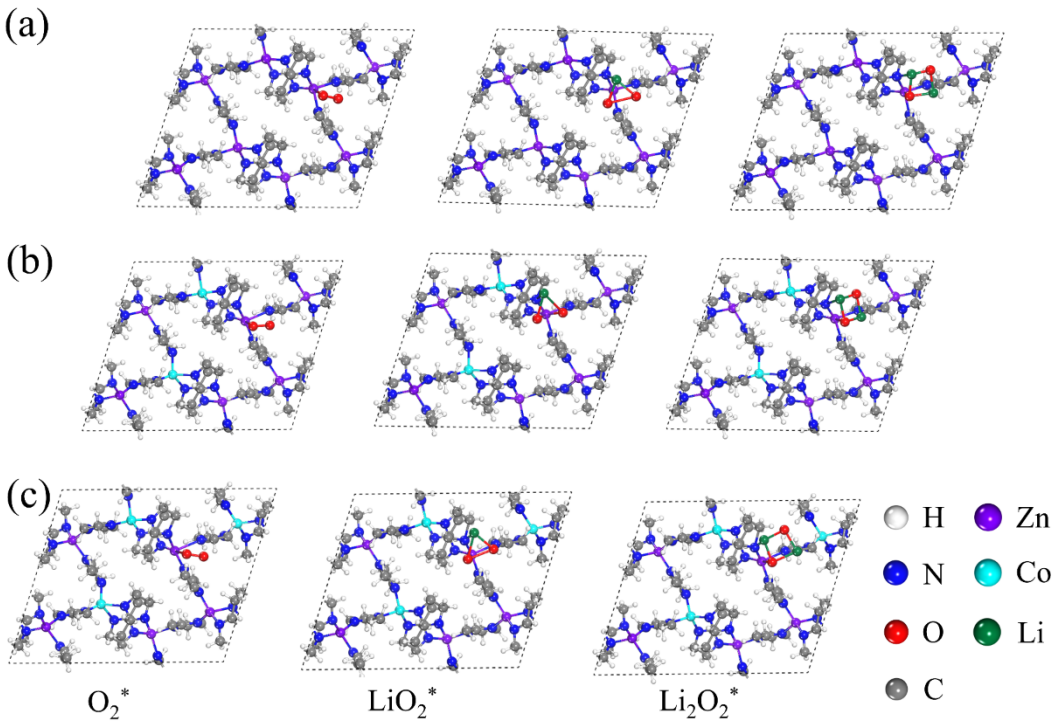

Figure S5. The optimize structure and adsorption energy of O_2, LiO_2, Li_2O_2 on (a) Zn ZIF, (b) $Zn_{0.8}Co_{0.2}$ ZIF and (c) $Zn_{0.6}Co_{0.4}$ ZIF.

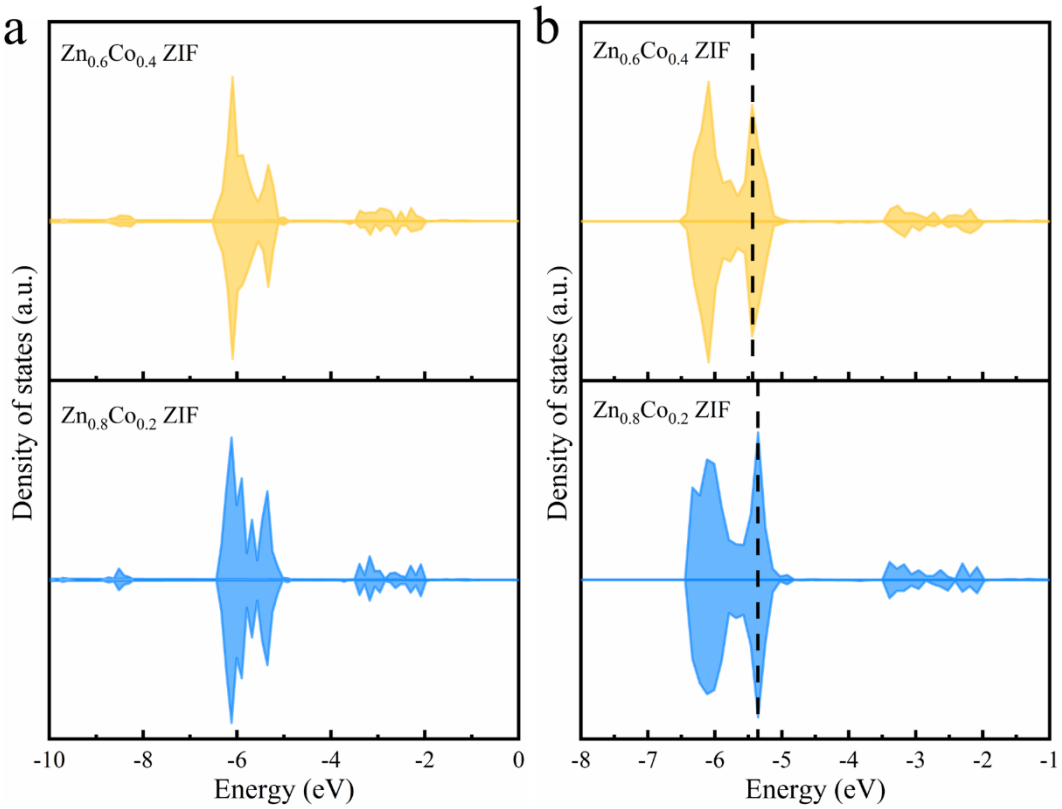

Figure S6. The PDOS of Zn $3d_{yz}$-orbital (a) and $3d_{xz}$-orbital (b) of $Zn_{0.8}Co_{0.2}$ ZIF and $Zn_{0.6}Co_{0.4}$ ZIF.

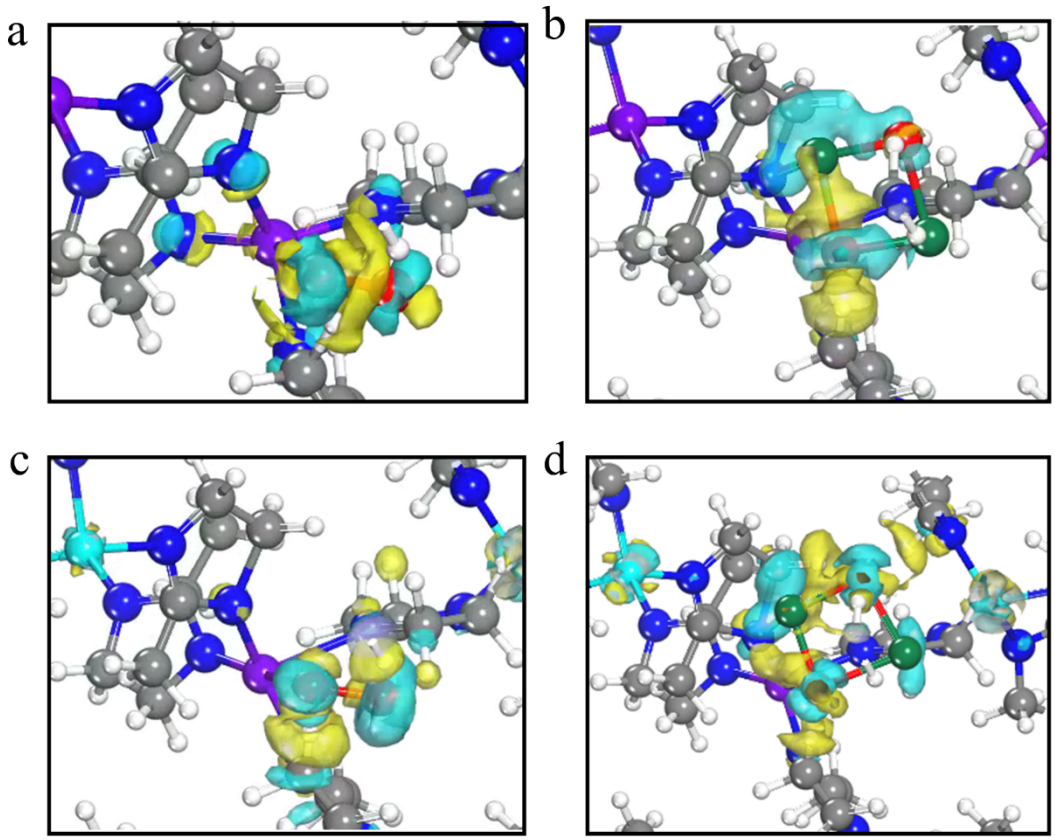

Figure S7. The differential charge density plots of O_2 and Li_2O_2 adsorbed on Zn ZIF (a) and (b) and $Zn_{0.6}Co_{0.4}$ ZIF (c) and (d). The charge density of yellow and blue represents the electron accumulation and depletion region, respectively.

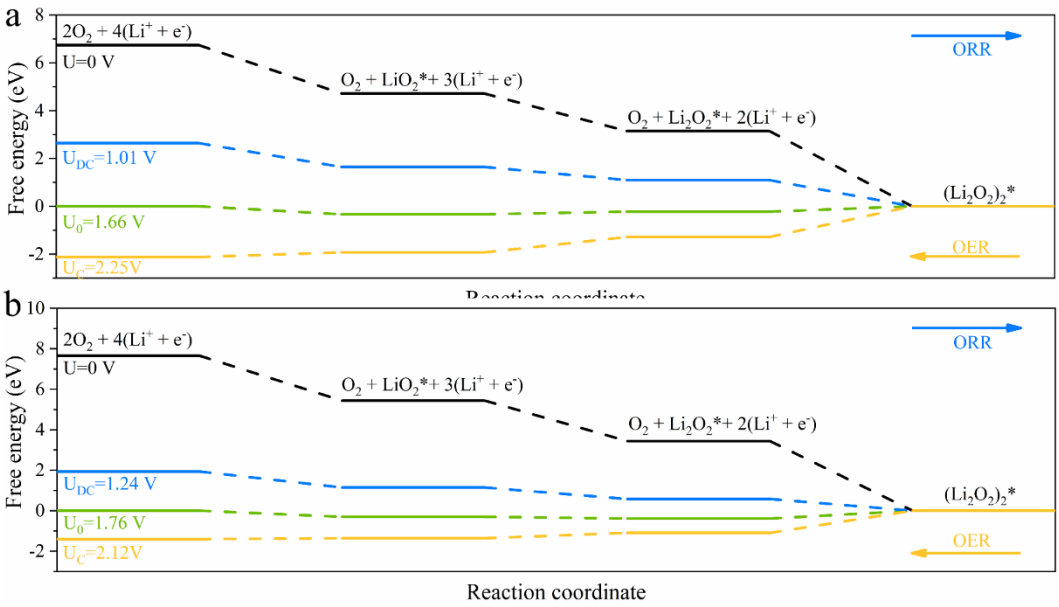

Figure S8. The free energy of ORR/OER on Zn sites for (a) Zn ZIF and (b) $Zn_{0.6}Co_{0.4}$ ZIF.

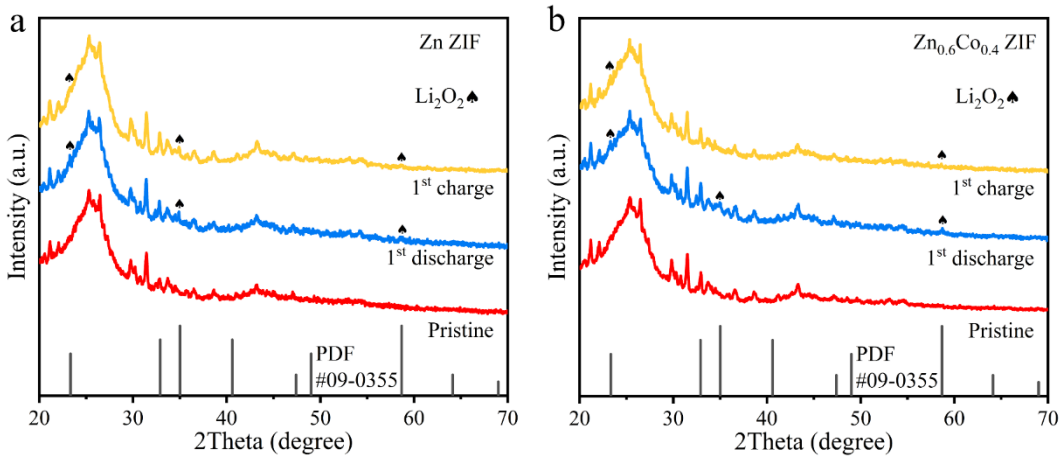

Figure S9. XRD pattern at different states for Zn ZIF electrode (a) and $Zn_{0.6}Co_{0.4}$ ZIF electrode (b).

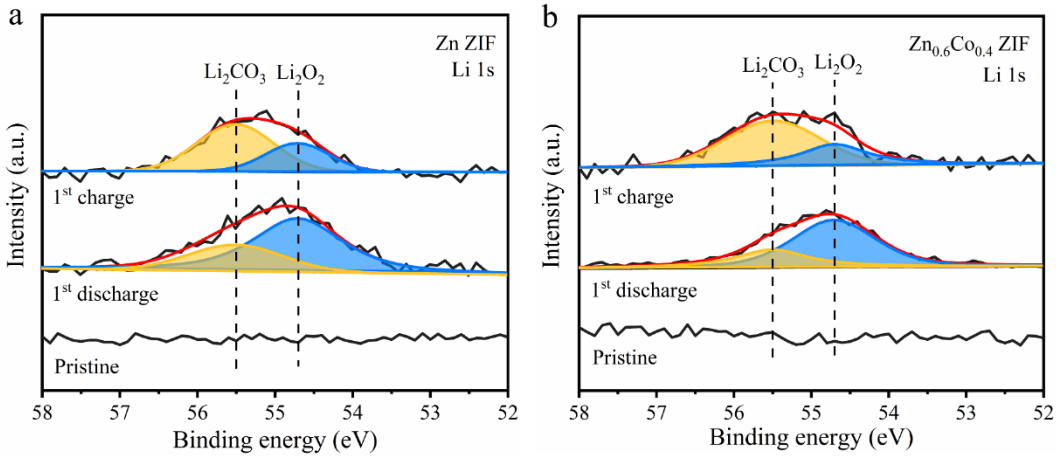

Figure S10. Li 1s XPS at different states for (a) Zn ZIF electrode and (b) $Zn_{0.6}Co_{0.4}$ ZIF electrode.

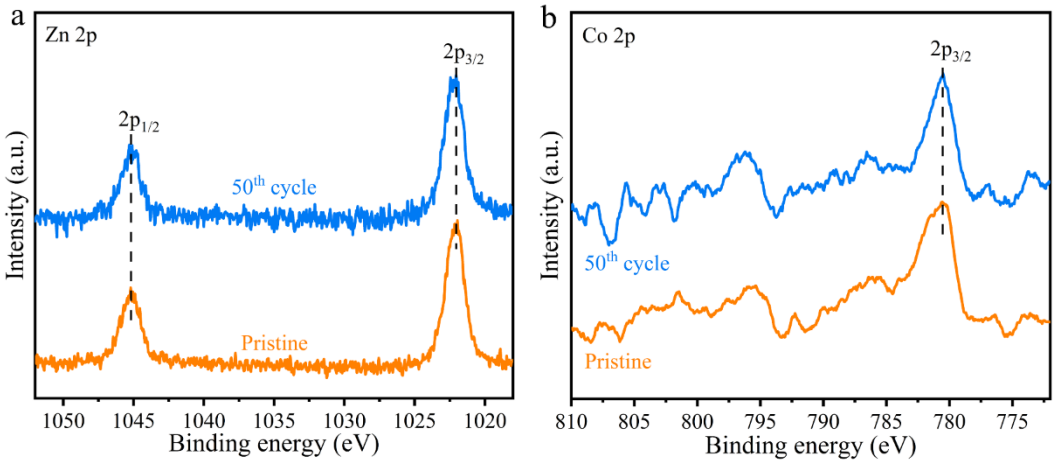

Figure S11. (a) Zn 2p and (b) Co 2p XPS for $Zn_{0.8}Co_{0.2}$ ZIF electrode after 50 cycles.

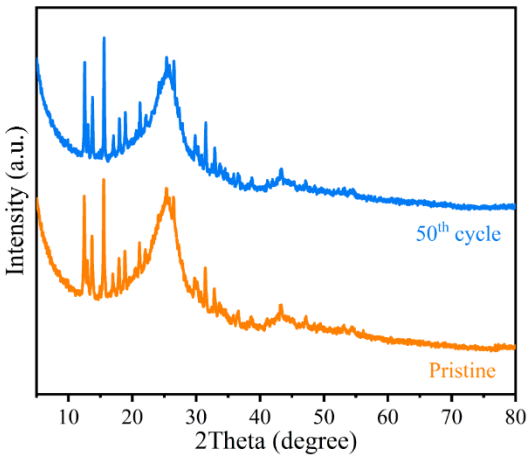

Figure S12. The XRD pattern for $Zn_{0.8}Co_{0.2}$ ZIF electrode after 50 cycles.

Table S1. The molar ratio of Zn and Co in total metal content for different as-papered samples calculated from the ICP-OES data.

samples	mass	element	Actual molar ratio of single metal in total metal content
$Zn_{0.8}Co_{0.2}$ ZIF	0.0191g	Zn	81.6%
		Co	18.4%
$Zn_{0.6}Co_{0.4}$ ZIF	0.0195g	Zn	61.9%
		Co	38.1%

Table S2. The Bader charge transfer from Zn sites of distinct electrocatalysts to reactant.

Configuration	Bader charge transfer from Zn sites to O_2	Bader charge transfer from Zn sites to Li_2O_2
Zn ZIF	0.415 e^-	0.593 e^-
$Zn_{0.8}Co_{0.2}$ ZIF	0.612 e^-	0.664 e^-
$Zn_{0.6}Co_{0.4}$ ZIF	0.583 e^-	0.624 e^-